Simulation and Parametric Study for the Hydrothermal Gasification of Palm Waste

by

Mohamed Hussein Malik Ahmed
15672

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2015

Universiti Teknologi PETRONAS
32610, Bandar Seri Iskandar
Perak Darul Redzuan

CERTIFICATION OF APPROVAL

Simulation and Parametric Study for the Hydrothermal Gasification of Palm Waste

by

Mohamed Hussein Malik Ahmed
15672

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

_____

Dr Nor Erniza Bt Mohammad Rozali

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

MOHAMED HUSSEIN MALIK AHMED

ABSTRACT

Leading and heading towards a renewable and sustainable society and community is a must in the modern world. The production of energy will play a big role in this process. One of the options for a renewable and sustainable energy is the production of hydrogen from palm waste as a biomass. Hydrothermal Gasification of biomass provides a highly efficient pathway to hydrogen production. The main objective of this project is to simulate the gasification model in order to know the effect of the temperature and steam/biomass ratio in the gas composition. Modeling and simulation approach allows to identify the potential alternatives for the optimal production of hydrogen. A simulation process will be adopted for achieving the desired objectives. The process under focus is hydrogen production from empty fruit bunch from oil palm via steam gasification with in-situ carbon dioxide capture by CaO as sorbent. The model incorporates the chemical reaction kinetics models of the steam gasification of EFB ($C_{3.4}H_{4.1}O_{3.3}$) and carbon dioxide adsorption, and the material balances. Parameter analysis on the influence of the temperature and steam/biomass ratio is performed. Increasing in temperature results in increasing of hydrogen and decreasing in methane and carbon dioxide. Increasing the steam/biomass ratio leads to increase of hydrogen and decrease of methane, carbon dioxide and carbon monoxide.

ACKNOWLEDGEMENT

In completion of this project, I would like to express my gratitude to all those who gave me the possibility and support to complete this Final Year Project dissertation and the whole implementation of this project. I owe my deepest gratitude to Allah The Most Gracious for the accomplishment of this final year project and to whom I owe my very existence. I offer my greatest appreciation to my respected and caring supervisors, Dr.Nor Erniza Bt Mohammad Rozali and Dr.Abrar for the supervision, guidance, advice and support throughout the project. Without their intensive encouragement, I would not be able to complete the project successfully. My gratitude also goes to mr. Shahbaz, the PhD student who has been helping me during this project. My deepest gratefulness is also expressed to my lovely parents, family and friends for their endless support and motivation which driven me to complete this project.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1
INTRODUCTION

1.1 Background of Study

The traditional fossil fuels (oil, coal and natural gas) continue to be the major sources of energy in the world. The increasing energy demands will speed up the exhaustion of the finite fossil fuel. Depending of fossil fuels has led to serious energy crisis and environmental problems, i.e. fossil fuel exhaustion and pollutant emission. Carbon dioxide is the main greenhouse gas, and a major part of CO_2 emissions is due to combustion of fossil fuels. In addition, combustion of fossil fuel produces toxic gases, such as SO_2, NO_x and other pollutants, causing global warming and acid rain. Scientists globally have shifted their effort towards developing alternative sustainable fuels and quite a number of technologies have been discovered. Several researches have been made to explore clean, renewable alternatives. One potential alternative solution is to produce energy from hydrogen as its energy content per kilogram is larger than that of gasoline. As hydrogen is clean and renewable source of energy, it can replace the conventional fossil fuels. A part from its use as a source of energy, hydrogen can be used for various other purposes in different industries. It is used in hydrogenation process, saturate compounds and crack hydrocarbons. It is a good oxygen scavenger and can therefore be used to remove traces of oxygen. It is also used in manufacturing of different chemicals like ammonia, methanol etc.

Being the world largest producer of palm oil, the potential for hydrogen production in Malaysia is logical due to the abundance of biomass. Empty fruit bunch (EFB) constitutes 23 % of the amount of palm waste. Among the thermo-chemical processes that can convert biomass into hydrogen are pyrolysis and gasification. Between the two, gasification offers lower production cost. Pyrolysis converts biomass to bio-oil prior to hydrogen. Meanwhile, gasification directly

converts biomass to hydrogen. Gasification is a process that converts organic or fossil based carbonaceous material into a combustible gas by reacting the material at high temperature with a controlled amount of air/oxygen often in combination with steam. Fluidized bed gasifiers are advantageous for gasification of biomass because of their flexibility in feedstock size and better contact between gases and solid. The objectives of this work are to develop the process to produce hydrogen from EFB via oxygen-steam gasification with in-situ adsorption of CO_2 using CaO, to perform simulation for the developed flowsheet in Aspen HYSYS.

1.2 Problem Statement

Hydrogen plays a big and important role in our energy future production. By optimizing the production of hydrogen, the dependence on the petroleum derived resources will be reduced. Modeling and simulation approach allows to identify the potential alternatives for the optimal production of hydrogen. That's why the way of getting higher amount of hydrogen should be known by using simulation programs before getting into experimental work. Experimental work usually is expensive and dangerous to deal with. By using simulation softwares such as Icon or HYSYS, simulation process can be made easily, extensive studies for the process and the parametric of the process will be made.

1.3 Objectives

The main objective of this project is to know the gas composition from hydrothermal gasification of EFB as a palm waste by:

- Developing a simulation model for the hydrothermal gasification of EFB.
- Performing a parametric study (temperature and steam/biomass ratio) in the developed simulation model.

1.4 Scope of Study

Biomass gasification in producing a hydrogen rich product has attracted great attentions in recent years. Apparently, the way to force the biomass gasification process into shift towards the maximum hydrogen rich end product is becoming a priority topic.

In order to know the hydrogen production amount and other gases produced from hydrothermal gasification process which is our objective, HYSYS simulation software will be used as it is easy to deal with, extensive parametric studies can be made and time and money will be saved. Empty fruit bunch (EFB) is used as a biomass and the parameters that are used in this study are temperature and steam/biomass ratio.

CHAPETER 2
LITERATURE REVIEW AND THEORY

Leading and heading towards a renewable and sustainable society and community is a must in the modern world. The production of energy will play a big role in this process. One of the options for a renewable and sustainable energy is biomass [1].

Catalytic Hydrothermal Gasification of biomass provides a highly efficient pathway to medium-Btu fuel gas. This gas product can be used directly in heat and power applications or has potential to be cleaned to pipeline quality gas. As a fuel gas, it could be used in the ethanol bio-refinery to displace other energy requirements [2].

2.1 Historical Overview of Hydrothermal Technology Development

Here the focus on an overview of the most significant pilot plant work and known or claimed commercial activities.

In the 1970's and 1980's the interest in alternative energy sources, such as biomass, was high due to the oil crises. The liquefaction research started in 1971 by the US Bureau of Mines18 with conversion of carbohydrates in hot compressed water in the presence of CO and Na_2CO_3. This combination of CO and Na_2CO_3 was considered necessary in the early developments for producing hydrogen in situ, until studies showed that the use of CO in combination with alkali leads to a limited increase in the oil yield [3].

2.2 Conceptual Process Design and Life Cycle Assessment

Conceptual process design has traditionally been used to optimize process configurations i.e., a list of interconnected equipment with defined sizes and operating conditions using cost and efficiencies as objectives. Life cycle assessment (LCA) allows evaluation of the environmental performance of a process and its entire life cycle, but has mainly been used to compare process options [4].

2.3 Hydrothermal Gasification of Waste Biomass

The hydrothermal gasification process upgrades biomass to hydrogen as an energy carrier while avoiding common issues of biomass conversion, which are linked to its energy intensive production and high moisture content. Given that methane is a gas essentially insoluble in water, the need to separate it from water using a distillation process is completely avoided, unlike the separation of ethanol from a water-rich fermentation product stream in the corn-grain to ethanol conversion process. A catalytic hydrothermal gasification process was developed at the Paul Scherrer Institut (PSI) in Villigen, Switzerland that allows for the production of methane from woody biomass. This process is carried out in an aqueous system at conditions near or above the critical point of water: 647 K (374 °C) and 22.1 MPa [5].

This process also avoids having to dry the starting product, thereby increasing energy efficiency, especially for wet biomass. Additional research is being done to adapt this process for a manure feedstock. In salt-containing feedstocks such as manure, salts must be separated prior to catalytic methanation to achieve long catalyst lifetimes. These salts can potentially be revalorized as a fertilizer. Both wood waste and manure were selected for further study as they represent residual biomass and, thus, avoid an energy intensive agricultural production process [5].

Figure A.1 in appendix A, shows the overview of the flowsheet (left section) and life cycle inventory flow model (right section) used for the simulated biomass conversion. The flow sheet model constitutes one of the stages of the life cycle inventory model.

2.4 Hydrogen

Hydrogen gas was first artificially produced in the early 16th century, via mixing of metals like zinc with dilute acids. Henry Cavendish in 1766 was first to recognize the gas. He called this gas as inflammable air since it burned when ignited. Later, Lavoisier found that the gas would produce water when burned, a property which later gave it its name as "Hydrogen" (Greek: Hydru = water forming). At standard temperature and pressure, hydrogen is a colorless, odorless, nonmetallic, tasteless and highly combustible diatomic gas with molecular formula H_2 [6].

2.5 Hydrogen Applications

Hydrogen can be used for various applications covering many industries [7]:

- Petroleum and chemical industries, like fossil fuels processing, ammonia manufacturing and petrochemicals (hydrodealkylation, hydrodesulfurization and hydrocracking).
- Hydrogenation agent to increase the level of saturation of unsaturated fats and oil.
- Metal production and fabrication.
- Shielding gas in welding methods such as atomic hydrogen welding.
- Rotor coolant in electrical generators at power stations.
- Production of float glass.
- Filling gas in balloons and airships.
- Energy storage technology.
- Electronic industry.
- Production and processing of silicon.
- Pharmaceuticals.
- Fuel for rocket propulsion.
- Power generation with fuel cells.
- Transportation sector.

2.6 Energy Production Processes from Biomass

The main routes for biomass conversion into energy are bio-chemical/biological processes and thermo-chemical processes. The first route is attractive due to lower secondary pollution generated from microorganism conversion method. however, major drawbacks from the processes are difficult to culture microorganism, low hydrogen generation efficiency and higher operating temperature needed to operate.

Figure 2.1 below shows the energy production processes based on biomass. Gasification is going to be the thermochemical process in order to produce the hydrogen gas [8].

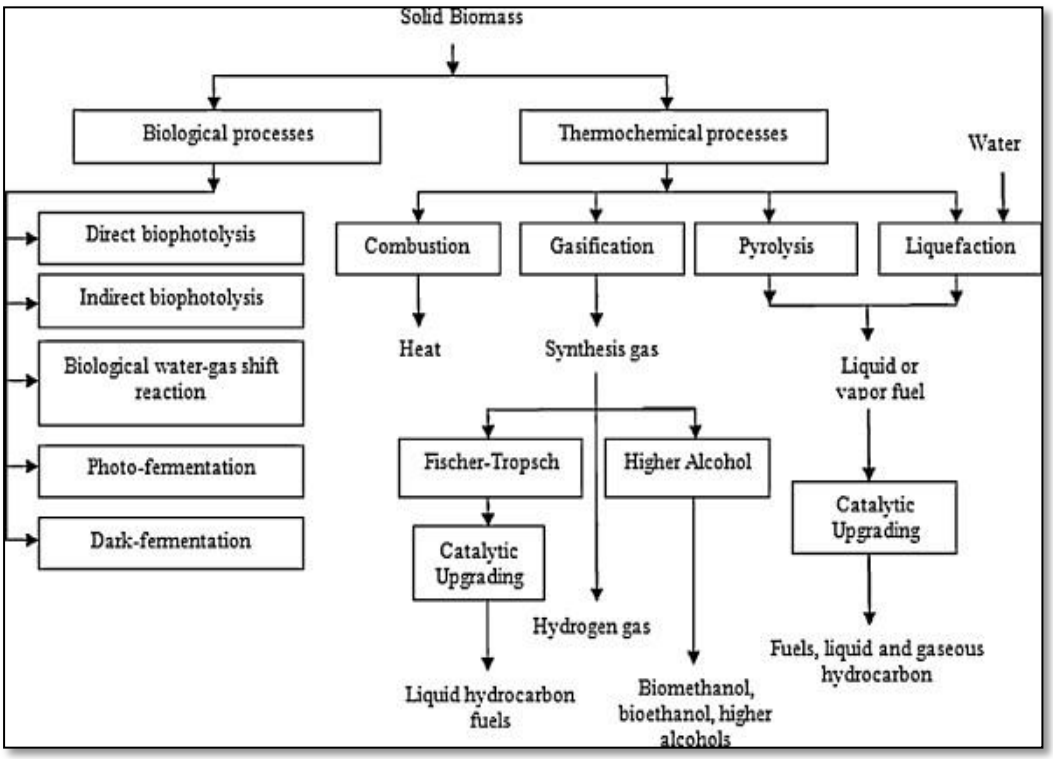

FIGURE 2.1 Energy production processes based on biomass

2.7 Oil palm waste in Malaysia

Oil palm is one of the major economic crops in many countries. Malaysia alone produces about 47% of the world's palm oil supply and can be considered as the world's largest producer and exporter of palm oil (Figure 2.2) [9].

Malaysia also generates huge quantity of oil palm biomass including oil palm trunks, oil palm fronds, empty fruit bunches (EFB), shells and fibers as waste from palm oil fruit harvest and oil extraction processing. At present there is a continuously increasing interest in the utilization of oil palm biomass as a source of clean energy. One of the major interests is hydrogen from oil palm biomass. Hydrogen from biomass is a clean and efficient energy source and is expected to take a significant role in future energy demand due to the raw material availability [10].Figure 2.2 below shows the world palm oil production in the year 2009. Malaysia has the highest oil production with a percentage of 47% of the world's palm oil supply.

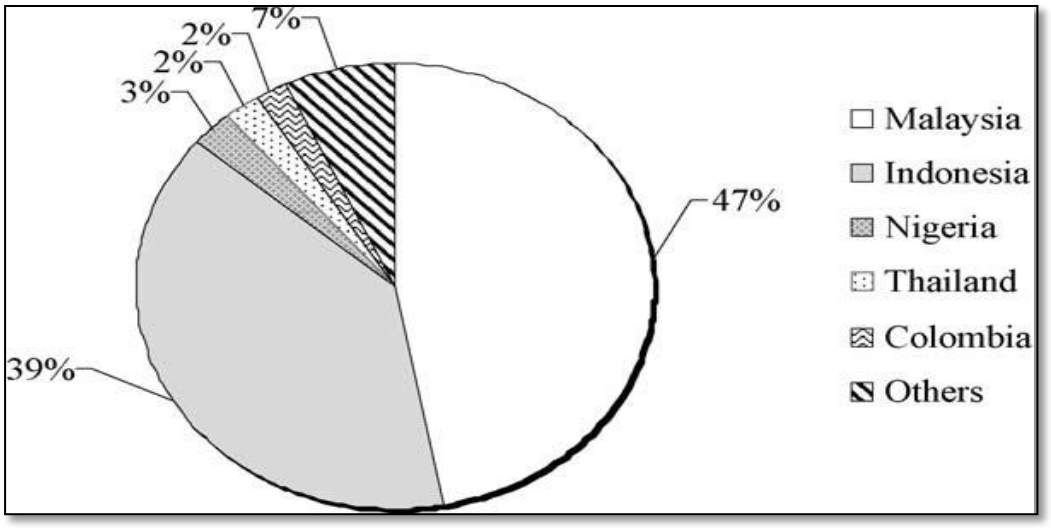

FIGURE 2.2 World palm oil production in the year 2009

2.8 Gasification

Unlike pyrolysis, gasification is the conversion of biomass into combustible gas mixture at high temperature range of 700–1000 °C, with a controlled amount of oxygen and/or steam (partial oxidation). The resulting gas mixture is called synthesis gas or syngas. This conversion process is expressed as:

$$\text{biomass}+\text{heat}\rightarrow H_2+CO+CO_2+CH_4+\text{hydrocarbon}+\text{char} \quad (1)$$

The oxidant agent can be air, hydrogen, steam, CO_2 or their mixtures. Air is a cheap and widely used as a gasifying agent, containing a large amount of nitrogen,

which reduces the heating value of the syngas produced . Usage of oxygen as a gasifying agent could produce a better quality syngas of medium heating value, but it requires a pure oxygen supply which leads to simultaneous problem of cost and safety . The use of CO_2 as the gasifying agent is promising because of its presence in the syngas. CO_2 with a nickel-based catalyst can convert char, tar and CH_4 into H_2 and/or CO, thus leading to higher amount of H_2 and CO contents in the syngas produced. If steam is used as the gasifying agent, the heating value and H_2 content in the syngas can be increased, however, the operational costs will also be increased due to the demand for an external heat source for steam production [11].

During the gasification process a number of exothermic and endothermic reactions take place. Heating and drying are endothermic processes, requiring a source of heat to drive them. This heat can be supplied by an external source in a process called indirectly heated gasification. More typically, a small amount of air or oxygen is admitted for the purpose of partial oxidation, which releases sufficient heat for drying and pyrolysis as well as for the subsequent endothermic chemical reactions. During gasification, physical, chemical and thermal processes may take place sequentially or simultaneously, depending on the reactor design and the feedstock.

Gasification is a solid-gas reaction converting solid carbon into gaseous CO, CO_2, H_2 and CH_4. Gasification reactions can be represented by [12]:
Combustion reaction:

$C + 1/2O_2 \rightarrow CO$ (2)

$CO + 1/2O_2 \rightarrow CO_2$ (3)

$H_2 + 1/2O_2 \rightarrow H_2O$ (4)

Boudouard reaction: $C + CO_2 \leftrightarrow 2CO$ (5)

Water gas reaction: $C + H_2O \leftrightarrow CO + H_2$ (6)

Methanation reaction: $C + 2H_2 \leftrightarrow CH_4$ (7)

Water-gas shift reaction: $CO + H_2O \leftrightarrow H_2 + CO_2$ (8)

Steam methane reforming reaction: $CH_4 + H_2O \leftrightarrow CO + 3H_2$ (9)

2.9 Hydrogen from gasification

Gasification is an important process for recovering energy from biomass. During gasification process, biomass is thermally decomposed to small quantities of char, liquid oil and high production of gaseous products under limited presence of oxygen. The product yields and the composition of gases are dependent on several parameters including temperature, gasifying agent, biomass species, particle size, heating rate, operating pressure, equivalence ratio, catalyst addition and reactor configuration.

Several research groups studied the gasification of biomass under different conditions using different types of catalyst to get the maximum hydrogen yield with different types of reactor. The catalysts used in biomass conversion could be divided into two groups which depend on the position of the catalyst in the gasification process. The first group is known as primary catalysts, where the catalysts are dry mixed with biomass feedstock or by wet impregnation, while the second group of catalysts is secondary catalyst, where the catalysts are placed on downstream from the gasifier [13]. Dolomite and CeO_2/SiO_2supported Ni, Pt, Pd, Ru and alkaline metal oxides can catalyze the gasification process to reduce tar formation and improve gas production quality and conversion efficiency [14]. Although $Rh/CeO_2/SiO_2$ has been reported to be the most effective catalyst reducing tar formation, nickel-based catalysts are highly active for tar reduction [15]. A summary of gasification biomass research using primary catalysts is shown in Table B.1 in appendix B.

TABLE 2.1 The gasification in supercritical water of different biomass for the production of hydrogen using different types of catalysts

Biomass	Catalyst	Reactor type	Reaction temperature (°C)	Pressure (MPa)	Hydrogen yield
Glucose	Ni/_Al_2O_3 Ni/CeO_2–_Al_2O_3	Autoclave	400	24.5	12.7 molH_2/kg feed
Glucose	R-nickel	Batch microreactor	340–380	15–25	6mmolH_2/g feed
Glucose	Ni/activated charcoal	Packed bed	575–725	28	2.45 molH_2/mol feed
Lignin	$RuCl_3/TiO_2$	Tubular	400	37.1	–
Paper sludge Black liquor	Alkali salts	Tubular	500–650	25	24 molH_2/kg feed
Cellulose	K2CO_3 $Ca(OH)_2$	High pressure autoclave	450-500	24–26	8.2 molH_2/kg feed
Cellulose sawdust	CeO_2, Ru/C (CeZr)xO_2	Tubular	500	27	4 gH_2/100 g feed

A summary of gasification biomass in supercritical water of different biomass for the production of hydrogen using different types of catalysts is shown in table 2.1.

2.10 Model for Biomass Gasification (Biomass Gasifier Model)

The gasifier has a bubbling fluidized bed of sand particles and a freeboard zone. Biomass is continuously fed into the reactor with steam as the gasifying agent. The gasifier operates at atmospheric pressure and high temperature. Biomass can be finally converted to fuel gases through primary pyrolysis, tar cracking, and other chemical reactions taking place in the gas and solid phases. A one-dimensional nonisothermal model is developed for modeling the biomass gasifier. The model considers that there are a particle-free bubble phase and an emulsion phase in the bubbling fluidized bed. The emulsion phase, containing all the particles and a fraction of the gases, is maintained at incipient fluidization conditions. The gas in excess of the amount needed to maintain the incipient fluidization conditions in the emulsion phase is considered to pass through the bed as bubbles. Figure 2.3 below shows the integration process for hydrogen production with the schematic bubbling fluidized bed gasifier [15].

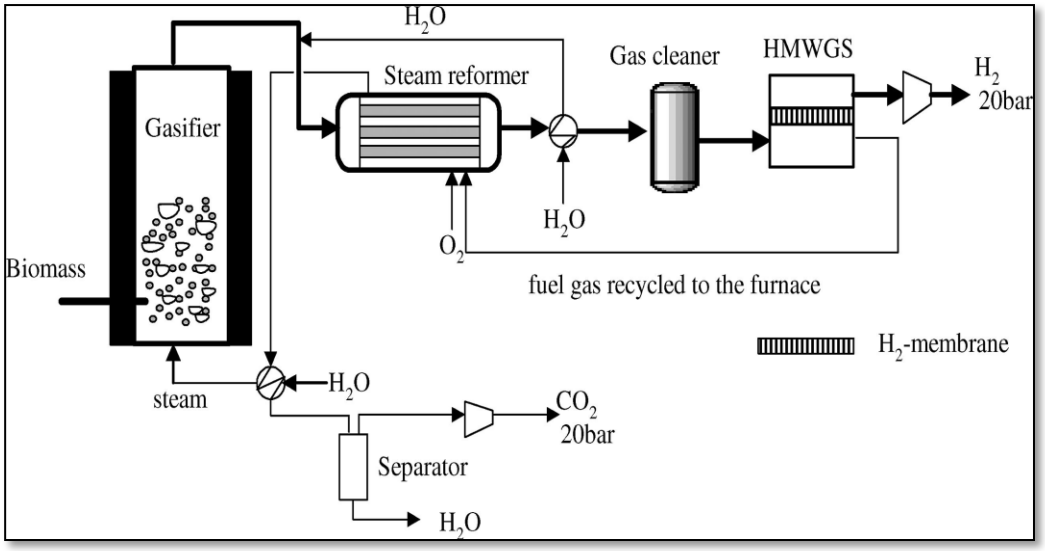

FIGURE 2.3 The integration process for hydrogen production

2.11 Atmospheric Fluidized Bed Simulation

One of the simulations of biomass gasification using ASPEN PLUS software has been done by Nikoo and Mahinpey [16]. The gasification equipment and gasification agent that they use is fluidized bed reactor and steam. They present the details of the modelling approaches taken to obtain a process simulation program for biomass gasification in a fluidized bed reactor. The following assumptions were considered in modelling the gasification process [17]:

a) Steady state and isothermal process.

b) Biomass devolatilization takes place instantaneously.

c) All gases are uniformly distributed within the emulsion phase.

d) Particles are spherical and of uniform size and the average diameter remain constant during gasification.

e) Char only contains carbon and ash.

Char gasification starts in the bed and completes in the freeboard. The following assumptions were made in simulating the hydrodynamics:

a) Fluidized reactor is divided into 2 regions (bed and freeboard).

b) The fluidization state in the bed is maintained in the bubbling regime.

c) The volume fraction of solids decreases as height increases.

d) Volumetric flow rate of gas increases along with height.

e) The mixing of ash, char particles and bed material.

f) The reactor is divided into a finite number of equal elements with constant hydrodynamic parameters.
g) The fluidized bed is one-dimensional (variations only occur in the axial direction).

A comprehensive simulation diagram for the fluidized bed gasification system is given in Figure 2.4. The experimental setup parameters used in the simulation were illustrated in Table B.2 which is shown in the appendix B.

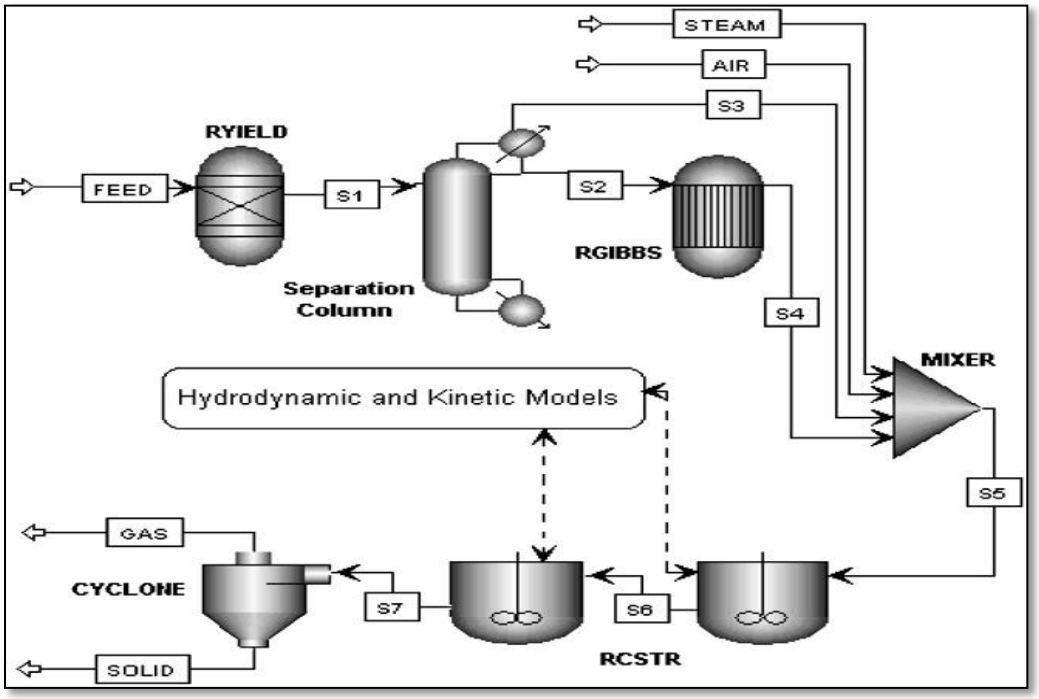

FIGURE 2.4 Simulation Diagram for the Fluidized Bed Gasification System

Hydrogen composition that obtained in this research paper were around 40-50 mol% and the highest hydrogen composition was at 900°C of reactor temperature. Increasing in reactor temperature had decreased the composition of carbon monoxide and methane but the composition of carbon dioxide showed contrast trend. Biomass produces more tar and unburned hydrocarbon in lower temperature, which decreases hydrogen production. Corresponding to steam gasification reaction, the higher amount of hydrogen favours the backward reaction. Furthermore, the backward reaction (steam gasification) dominates the prediction of carbon monoxide and it shows slight underestimation in temperatures lower than 800°C. Hydrogen composition increases when the steam/biomass ratio increases. The percentage of

hydrogen in product gas is the best precision for gasification without steam because of the low amount of tar in the process. Higher flow rate of steam decreases carbon monoxide and increases carbon dioxide in the product gas [18].

CHAPTER 3
METHODOLOGY

3.1 Project Flow Chart

The estimated work flow throughout this project is summarized in the schematic flow diagram as shown in figure 3.1:

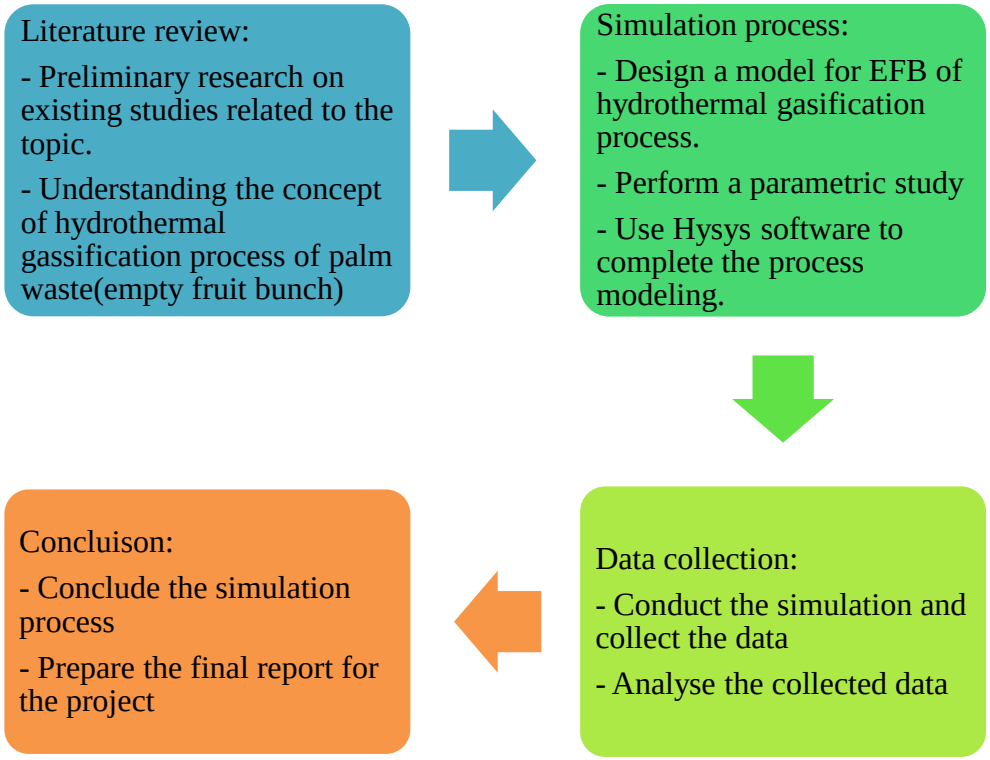

FIGURE 3.1 Flow diagram of the project

3.2 Process Description

The block flow diagram used in this study is shown in Figure 3.2. The Empty Fruit Bunch (EFB) was pre-treated before going to gasification. In the present work, the reactor temperature was increased from 650 °C to 900°C in 50°C increments to investigate the effect of temperature on gas composition and hydrogen yield and the results referring only to steam/biomass ratio of 0.6. The effects of the steam/biomass ratio on hydrogen production from biomass gasification were also studied. The steam/biomass ratio was varied by changing the steam flow while keeping the biomass flow constant at a temperature of 750°C. Drying was used in order to remove the moisture and the EFB was by that turned into small particles. The EFB and sorbent were fed into the gasifier at atmospheric temperature. The steam produced in a steam generator was superheated and then sent to the system. The gasification process was combined with CO_2 adsorption step and six major reactions listed in Table 3.1 are taking place in the gasifier. As the steam gasification process is endothermic, external energy was supplied. Fly ash and other solid particulates were removed from the product gas using a filter. The gasifier gas (CO, CO_2, H_2, CH_4) reacts with steam to produce H_2 and CO. Successively, the resulting H_2 rich gas was then compressed and fed into an adsorption unit. Finally a pressure swing adsorption (PSA) unit was used to purify the product gas to achieve 99.99 % pure hydrogen. Below is the block flow diagram shown in figure 3.2.

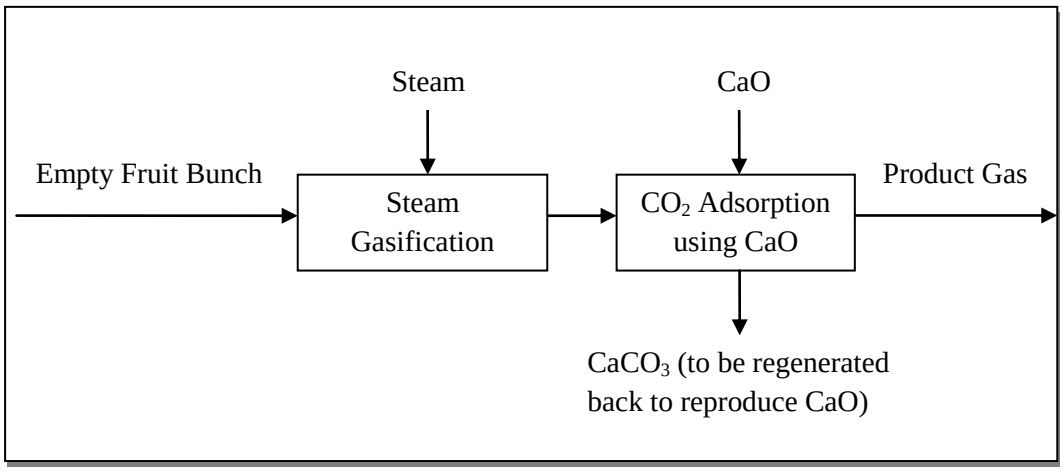

FIGURE 3.2 Block flow diagram for the gasification process

3.3 Model Assumptions and Reaction Kinetics

Below are the assumptions made in the process flowsheet development:

- EFB is represented as $C_{3.4}H_{4.1}O_{3.3}$ [19].
- The process operates under a steady state condition.
- The reaction isothermally at constant volume.
- Tar formation is negligible in the process.

There are six reactions occurring in the gasification process (as listed in Table 3.1), the carbonation reactions is assumed to be unidirectional and simulated as conversion reactions. The other reactions are in thermodynamic equilibrium. Due to limited kinetics data for EFB gasification, coal gasification kinetics modelling approach was applied [19].

TABLE 3.1 Reactions occur in the gasification process

Reaction	**Reaction Scheme**	K_o **[11] or Conversion**	ΔG_o
Gasification	$C_{3.4}H_{4.1}O_{3.3} + 0.1\ H_2O \leftrightarrow 2.15\ H_2 + 3.4\ CO$	3.139×10^{12}	16344
Boudouard	$C_{3.4}H_{4.1}O_{3.3} + CO_2 \leftrightarrow 4.4\ CO + 0.9\ H_2O + 1.15\ H_2$	1.238×10^{10}	20294
Methanation	$C_{3.4}H_{4.1}O_{3.3} + 8.05\ H_2 \leftrightarrow 3.4\ CH_4 + 3.3\ H_2O$	1.435×10^{11}	-11005
Methane reforming	$CH_4 + H_2O \rightarrow CO + 3\ H_2$	39.97	-
Water-Gas Shift	$CO + H_2O \leftrightarrow H_2 + CO_2$	-	-
Carbonation	$CaO + CO_2 \rightarrow CaCO_3$	Conversion = 99%	-

Here ΔG_o is Gibbs energy (J/kmol), K_o is equilibrium coefficient.

3.4 Gant Chart (FYPII) and Key Milestones

Table 3.2 below shows the targeted achievable timeline for Final Year Project II (FYPII).

TABLE 3.2 Gantt chart

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project work continuous	■	■	■	■	■	■	■	■							
2	Preparation and submission of progress report								●							
3	Project work continuous								■	■	■	■	■			
4	Pre-SEDEX											●				
5	Submission of Draft Report											●				
6	Submission of Soft Bound Dissertation												●			
7	Submission of Technical Paper												●			
8	FYP II Oral Presentation (VIVA)													●		
9	Submission of Hard Bound Dissertation															●

■ Progress
● Deliverable (Key milestone)

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Process Simulation Model in Hysys

The developed simulation model, as shown in Figure 4.1, incorporates the reactions listed in Table 3.1 and hence configured as if consisting of a partial oxidation reactor, a gasifier, a methane reformer, a water gas shift reactor, a carbonation reactor and a desorber. Pre-treated EFB, CaO and steam are fed into the gasifier. The first reaction involves EFB oxidization into CO_2 and water and this was modeled as a partial oxidation reactor. The products and unreacted feed next undergo steam gasification in which EFB was reacted with steam under constant pressure and temperature. This reaction produces hydrogen and CO and was simulated as an equilibrium reaction. Parallel to this reaction, Boudouard reaction also occured in the same reactor. Methanation was assumed to happen subsequently, and this reaction that occurs between EFB and hydrogen produces CH_4 and water. CH_4 was next cracked in a steam-assisted environment to produce hydrogen and CO as by-product. The equilibrium reaction of WGS between CO and steam next produces hydrogen and CO_2. The final reaction was the carbonation. The reaction of CO_2 with CaO was fed into the system. The hydrogen-rich product gas was to be further run through a separator which conceptually represents a pressure swing adsorption unit for hydrogen purification.

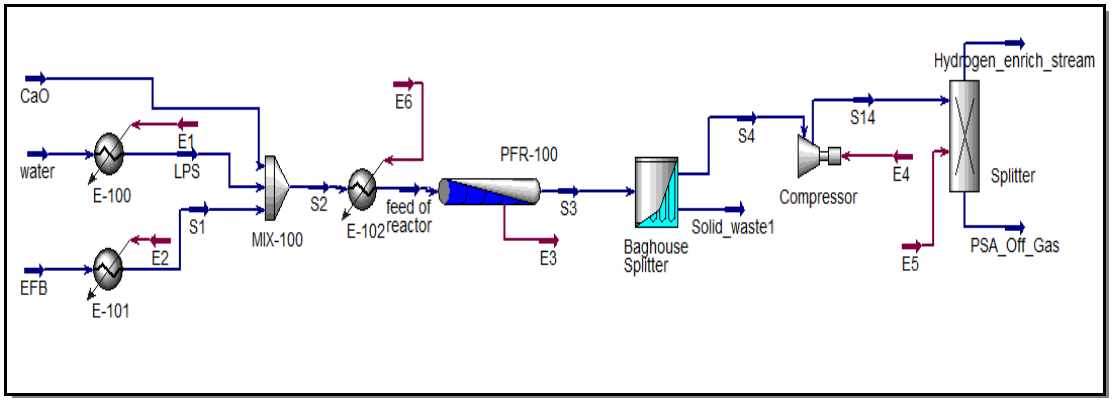

FIGURE 4.1 process flow diagram for the gasification process

4.2 Effect of Reactor Temperature

It is known that temperature plays an important role in biomass gasification. In the present work, the reactor temperature was increased from 650 °C to 900°C in 50°C increments to investigate the effect of temperature on gas composition and hydrogen yield and the results referring only to steam/biomass ratio of 0.6. The simulation results are presented in the figure below:

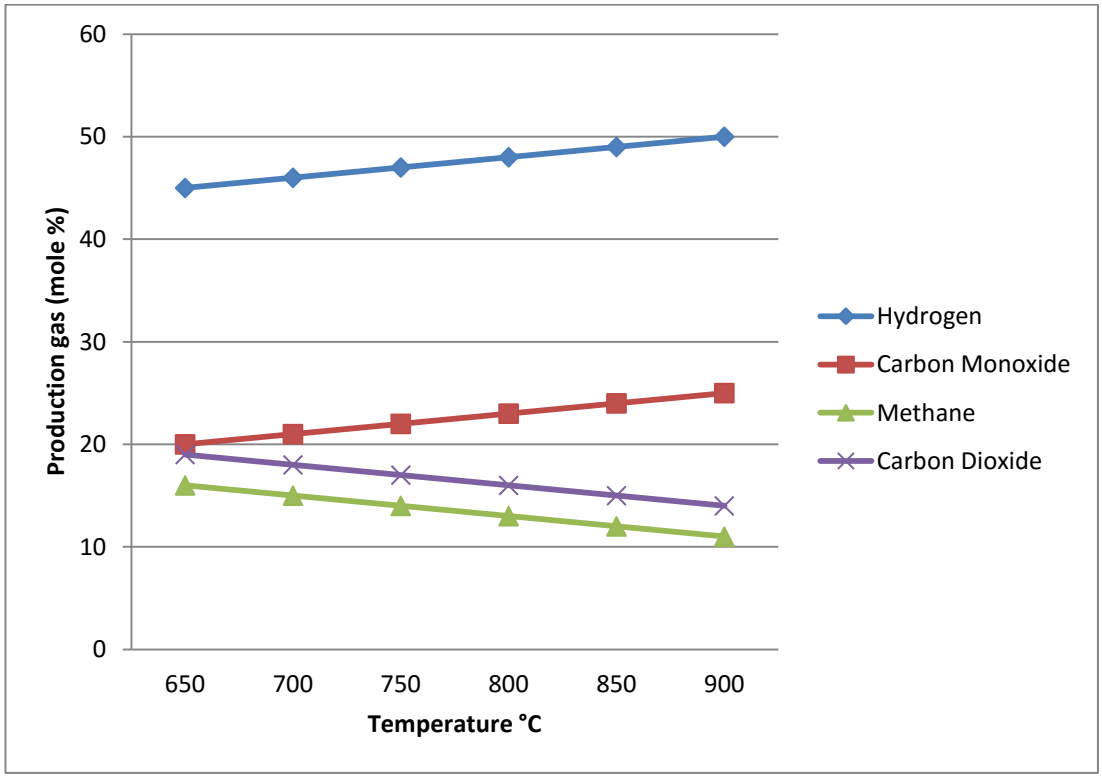

FIGURE 4.2 Effect of Gasification Temperature on Gas Composition of Empty Fruit bunch.

The gas composition is shown as a function of the gasifier temperature. The Hydrogen content was maintained around 40-50 mol% at the temperature range of 650-900°C. Research done by Shen also gets the similar result [20]. The gas yields increase with the increase in reactor temperature, whereas according to experimental result, the tar and char yields decrease. Higher temperatures favour the reactants in exothermic reactions and favour the products in endothermic reactions. Therefore, endothermic reactions (steam gasification, boudouard and steam reforming) were strengthened with the increasing temperature in the gasifier which resulted in increase of Hydrogen and Carbon Monoxide and decrease of Carbon Dioxide and

Methane [20]. At the same time, water gas shift reaction greatly determines the dry gas composition, which contributes to the increase in Hydrogen production. Moreover, this process is integrated with CO_2 adsorption, resulting in the deviation in the final compositions of the syngas, especially for CO_2. The Methane content in the dry gas slightly decreases infererred that Methane reforming is still difficult, even in elevated temperatures under experimental conditions [20].

4.3 Effect of Steam/Biomass Ratio

The effects of the steam/biomass ratio on hydrogen production from biomass gasification were also studied. The steam/biomass ratio was varied by changing the steam flow while keeping the biomass flow constant. The effect of the steam/biomass ratio on gas composition at the gasifier temperature of 750°C is shown in the figure below:

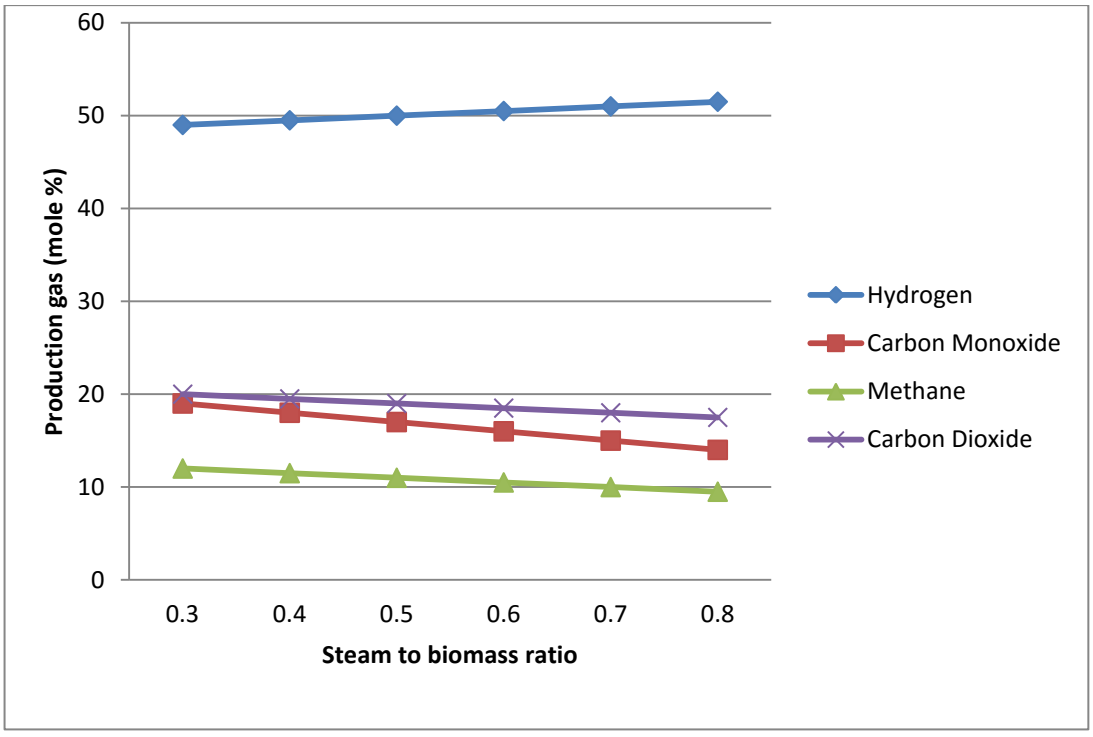

FIGURE 4.3 Effect of Steam/biomass ratio on Gas Composition of Empty Fruit bunch

As shown in figure 4.3, it is found that hydrogen composition increases with the increase in the steam/biomass ratio from 0.3 to 0.8 whereas the carbon monoxide, carbon dioxide and methane composition decreases. The observation is due to the enhanced CH_4 steam reforming and WGS reactions, which are highly dependent on steam feed rate. CO_2 decreases due to the carbonation reaction with CaO. This simultaneous removal of CO_2 shifts the equilibrium of water gas shift reaction to produce more hydrogen, resulting in hydrogen-rich product stream. It shows that, the addition of steam favours hydrogen formation. It can be inferred that the steam reforming reaction plays an important role in determining the dry gas composition and hydrogen production. As a result, hydrogen composition increased with the rise of the steam/biomass ratio [20].

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This project is important as it deals with the way to know the amount of hydrogen and the other gasses throw the hydrothermal gasification process of EFB as palm waste. Developing a simulation model for the hydrothermal gasification of palm waste has been made by using Aspen Hysys simulation software and the results were obtained and analyzed. Also a parametric study has been made. Increasing in temperature results in increasing of hydrogen and decreasing in methane and carbon dioxide. The highest amount of hydrogen production obtained was 50 mole % in a temperature of 900^{o}C and with a constant steam/biomass ratio of 0.6. Increasing the steam/biomass ratio leads to increase of hydrogen and decrease of methane, carbon dioxide and carbon monoxide. The highest amount of hydrogen production obtained was 52 mole % with a steam/biomass ratio of 0.8 and a constant temperature of 750^{o}C. Overall, all the objectives of the project were achieved, to simulate the gasification model in order to know the effect of the temperature and steam/biomass ratio in the gas composition.

5.2 Recommendation

For this project, extensive research has to be done regarding the properties of EFB in order to create a more accurate hypothetical component in Aspen HYSYS. Furthermore, detailed kinetics study on the EFB gasification reaction is needed to obtain more accurate results.

REFERENCES

[1] Thigpen, *Proc. 3rd Annual Biomass Energy Systems Conf.,* 5-7 June, Golden, Colorado, SERI/TP-33-285, 1979, pp.521.

[2] Craig, *Cost and Performance Analysis of Biomass-Based Integrated Gasification Combined-Cycle (BIGCC) Power Systems NREL/TP-430-21657* Golden, CO: National Renewable Energy Laboratory,1996.

[3] Goudriaan F, Thermal efficiency of the HTU Process for biomass liquefaction. In Proceedings of the conference: *Progress in Themochemical Biomass Conversion* (edited by Bridgwater, A. V.),Blackwell Science: England, 2000, pp 1312.

[4] Johnson, *Technology Assessment of Biomass Ethanol: a Multi- Objective, Life Cycle Approach under Uncertainty*; Massachusetts Institute of Technology: Cambridge, MA, 2006.

[5] Zah R, *Life Cycle Assessment of Energy Products: Environmental Assessment of Biofuels*; Federal Office of Energy: Bern, Switzerland, 2007.

[6] Saxena, *Thermo-chemical routes for hydrogen rich gas from biomass: a review,* Renewable and Sustainable Energy Reviews, 12, 2008, pp. 1909–1927.

[7] H.B. Goyal, *Thermochemical conversion of biomass to liquids and gas,* Monograph communicated to Haworth Press, USA, 2006.

[8] M. Ni; D.Y.C. Leung, *An overview of hydrogen production from biomass***,** Fuel Processing Technology, 87, 2006, pp. 461–472.

[9] Basiron Y, *Palm oil production through sustainable plantations*, European Journal of Lipid Science and Technology, 2007, 109:289–95.

[10] Umikalsom MS, *The treatent of oil palm empty fruit bunch fibre for subsequent use as substrate for cellulase production by Chaetomium globosum Kunze,* Bioresource Technology, 1997, 62:1–9.

[11] Rapagna S, *Steam-gasification of biomass in a fluidised-bed of olivine particles,* Biomass and Bioenergy, 2000, 19:187–97.

[12] Higman C, (2008) *Gasification Processes. Gasification. Second ed.* Burlington: Gulf Professional Publishing, 2008, pp. 91–191.

[13] Turn SQ; Kinoshita CM; Ishimura DM, (1997). *Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching,* Biomass and Bioenergy 1997.

[14] Rapagnà S; Jand N; Kiennemann A; Foscolo PU, (2000). *Steam-gasification of biomass in a fluidised-bed of olivine particles*. Biomass and Bioenergy 2000, 19:187–97.

[15] Asadullah M; Miyazawa T; Ito SI; Kunimori K; Tomishige K, (2003). *Catalyst performance of Rh/CeO2/SiO2 in the pyrogasification of biomass*. Energy and Fuels 2003, 17:842–9.

[16] Radmanesh, R.; Chaouki, J.; Guy, C, (2006) *Biomass gasification in a bubbling fluidized bed reactor: experiments and modeling*. AIChE J. 2006, 52, 4258–4272.

[17] Lewis WK and Gilliland ER, *Entrainment from fluidized beds*. Chemical Engineering Progress Symposium Series, 1962, 58:65–78.

[18] Aspen Technology, Aspen Plus 12.1 user guide. Cambridge, MA, 2003.

[19] K. Laohalidanond, J. Heil and C. Wirtgen, (2006). *The Production of Synthetic Diesel from Biomass,* KMITL Science and Technology Journal, Vol. 6, No. 1, Jan.-Jun., 2006.

[20] L. Shen, Y. Gao and J. Xiao, *Simulation of hydrogen production from biomass gasification in interconnected fluidized beds*. Biomass and Bioenergy. 32, 2008, 120-127.

APPENDICES

Appendix A

I. figure A.1

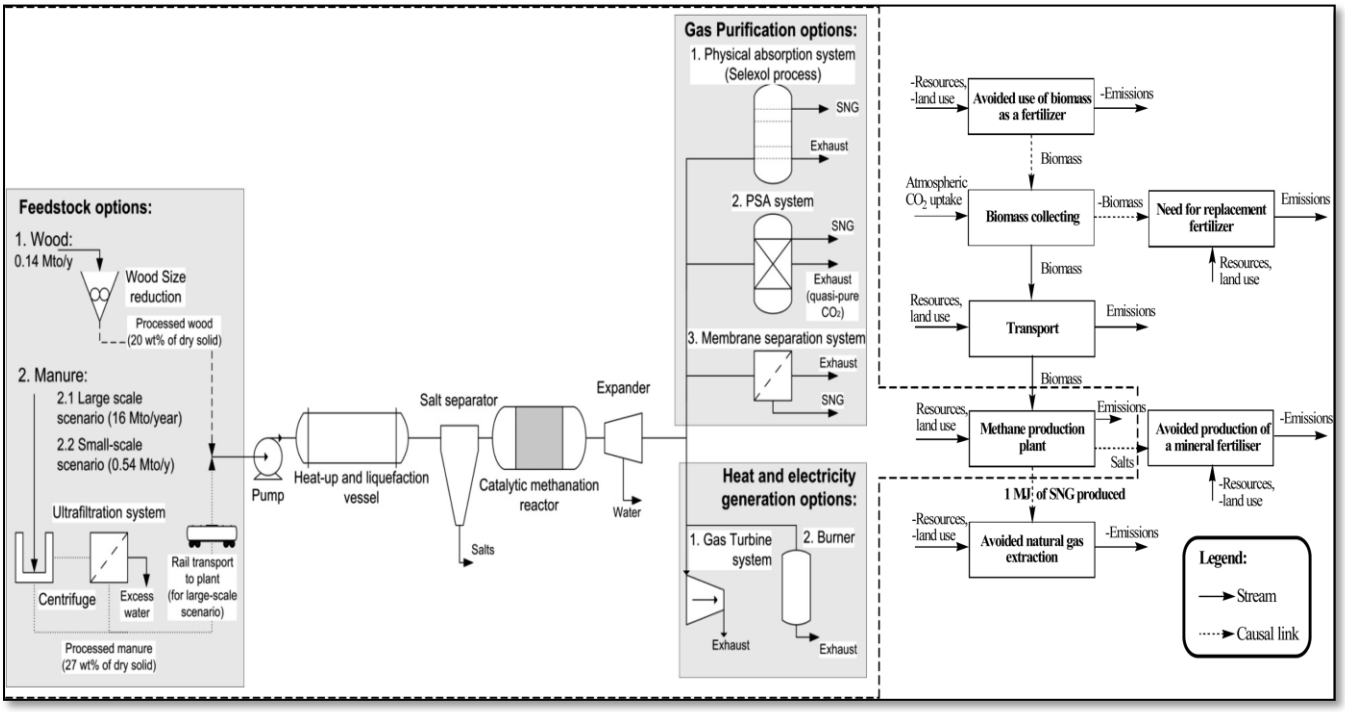

Figure A.1 Overview of the flowsheet (left section) and life cycle inventory flow model (right section).

Appendix B

I. Table B.1

Table B.1 The gasification of different biomass for the production of hydrogen using different types of catalyst (primary catalysts).

Biomass	Catalyst	Reactor type	Reaction temperature (°C)	Hydrogen yield
Almond shells	Olivine	Fluidized bed	770	52.2 vol.%
Spruce wood	Quartzite Olivine	Fluidized bed	780	31 vol.%
Cellulose	Rh/CeO_2	Fluidized bed	500–550	1290 μmol
Cellulose	$Rh/CeO_2/SiO_2$	Fluidized bed	600	38.66 vol.%
Cedar wood	$Rh/CeO_2/SiO_2(60)$	Fluidized bed	550–700	1207 μmol
Apricot stones	Olivine Dolomite	Fixed bed	800	22.9 mol H_2/kg biomass
Legume straw	Limestone	Free-fall	750–850	43 mol%
Pine sawdust	Olivine Dolomite			
Cedar wood Aspen	CaO	Tubular	850	29 cm^3/0.04 g biomass
Rice straw	Ni/olivine	Fluidized bed	800	31.5 vol.%
Wood	K_2CO_3	Fluidized bed	750	52.4 wt.%
Grape Olive bagasse	$ZnCl_2$	Cylindrical	600	2.4 mol/kg biomass
Bagasse	$Ni–Al_2O_3$	Fixed bed	800	51.7 vol.%
Biomass	Fe, NiO	Tubular	950	119 g H_2/kg bio mass
Biomass	Ni-based + calcium	Tubular	950	79.4 g H_2/kg bi omass

II. Table B.2

Table B.2 Parameters in Atmospheric Fluidized Bed Simulation

Reactor Temperature	700-900 C
Reactor pressure	1.05 bar
Bed diameter	40 mm
Freeboard diameter	60 mm
Reactor height	1400 mm
Air temperature	65 C
Air flow rate	0.5-0.7 N m3/h
Steam temperature	145 C
Steam flow rate	0-1.8 Kg/h
Silica sand average particle size	0.275 mm
Silica sand weight	30 g